

PROMISING NEW HIGH-EXPLOSIVES: TRIAMINO GUANIDINIUM (TAG) AND DINITRAMIDE (DN) SALTS

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ABSTRACT

High nitrogen energetic materials with astonishing thermal behaviors and performances were synthesized by different metathesis reactions. Particularly the new compound triaminoguanidinium 1-methyl-5-nitriminotetrazolate (TAG-1-Me-AtNO₂, **4**) shows great explosion performance and may be an alternative to commonly used and toxic RDX. An improved synthesis for the promising energetic compound **4** is also presented. The new compound TAG₂-OD (triaminoguanidinium 3,3'-bis-1,2,4-oxadiazol-5-onate, **7**) with an N-content of 60% and a relatively low isobaric (20 bar) combustion temperature of 1420 K may well be suitable for a N-rich component in erosion-reduced gun propellants.

The highly energetic compounds azidoformamidine dinitramide (AF_DN, **8**), 1,3,5-triaminoguanidinium dinitramide (TAG_DN, **9**) 5-aminotetrazolium dinitramide (HAT_DN **10**) were prepared in high yields according new syntheses by the reaction of potassium dinitramide and triaminoguanidinium, azidoformamidinium and 5-aminotetrazolium perchlorate, respectively. A full characterization of the chemical properties (IR and Raman spectroscopy, multinuclear NMR spectroscopy, mass spectrometry and elemental analysis) as well as of the energetic characteristics (differential scanning calorimetry, bomb calorimetry, impact, friction and electrostatic tests) is presented. The heats of formation were calculated (CBS-4M) in an extensive computational study. The detonation parameters of compound **8-10** were calculated using the EXPLO5 software: **9**: $D = 9039 \text{ m s}^{-1}$, $p = 320 \text{ kbar}$. Including the good thermal stability **9** could be an alternative to RDX as a high explosive. In addition, the thermal behavior under confinement and the performance was tested applying a "Koenen" steel sleeve test resulting in a critical diameter of $\geq 10 \text{ mm}$.

1. INTRODUCTION

Great strides have been made in increasing performance and decreasing sensitivity in energetic materials since the first commercialization of nitroglycerine (NG) in the form of dynamite in 1867 by

Alfred Nobel. However, the DoD continues to rely on traditional, half-century old energetics to meet their combat needs. New energetic materials have to be developed to maintain a lethality overmatch towards all enemies in the next stage of combat.

To effort this, promising new high explosives are needed. Current research in the field of high energetic materials achieve better results in power and avoiding pollution and health endangering problems of common explosives. Thus the research strategies aim on increasing nitrogen containing compounds. The 1,3,5-triaminoguanidinium cation has already proved its effectivity as high nitrogen building block in energetic materials.¹ Also the dinitramide anion can be found in some energetic materials like in the recently introduced FOX-12 (guanyl urea dinitramide, GUDN).² Combining these building blocks in one molecule increases explosive performance significantly. Simple syntheses with high yields as well as several interesting high nitrogen compounds based on the TAG⁺ and on the DN⁻ ions are presented in this work. The relevant energetic data are summarized in Table 8 and most important criteria are visualized in Fig. 3

2. TRIAMINO GUANIDINIUM SALTS

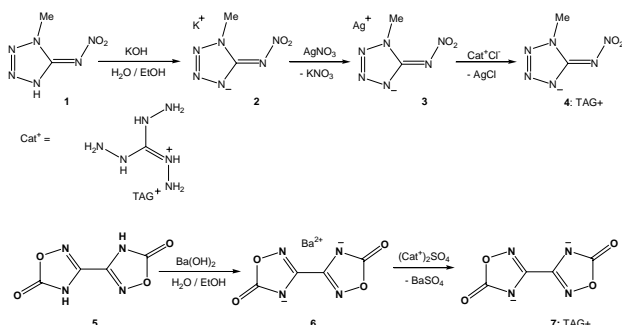
2.1. SYNTHESIS

Scheme 1 shows a general survey of syntheses of the 1,3,5-triaminoguanidinium 1-methyl-5-nitriminotetrazolate (TAG 1-MeAtNO₂) and 3,3'-bisoxadiazol-5-onate (TAG₂OD) salts. These compounds were synthesized using silver 1-methyl-5-nitriminotetrazolate (**3**) and barium 3,3'-bis-1,2,4-oxadiazol-5-onate (**6**), which was used in the wet state. **3** was obtained by metathesis reaction of potassium 1-methyl-5-nitriminotetrazolate (**2**) and silver nitrate. **6** was obtained by reacting barium hydroxide with the acidic 3,3'-bis-1,2,4-oxadiazol-5-onate. The reaction product 1,3,5-triaminoguanidinium 1-methyl-5-nitriminotetrazolate (**4**), was formed by the reaction of **3** with the correspondent chloride salts and (**7**) by the reaction of **6** with the correspondent sulfate. Thereby the impetus of these reactions is the formation of silver chloride and the barium sulfate, which feature a

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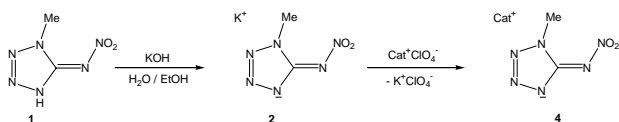
very low solubility in water and can be easily removed by filtration.

Scheme 1 Syntheses of compounds **4** and **7** via the formation of AgCl and BaSO₄.



An alternative procedure forming **4** is the reaction of the potassium salt **2** and the corresponding guanidinium perchlorates under the formation of low soluble potassium perchlorate. This method does not include an intermediate and therefore the reaction yields are slightly better and nearly quantitative. As the perchlorates are more sensitive than the chlorides, appropriate security measures have to be applied.

Scheme 2 Syntheses of compounds **4** via the formation of KClO₄.



A further facile route to **4** is the reaction of **1** with commercially available aminoguanidine bicarbonate, followed by addition of two equivalents of hydrazine hydrate, which results in an overall yield of > 82%.

2.2. SENSITIVITIES

The impact sensitivity tests were carried out according to STANAG 4489³ modified according to instruction⁴ using a BAM (Bundesanstalt für Materialforschung) drophammer.⁵ The friction sensitivity tests were carried out according to STANAG 4487⁶ modified according to instruction⁷ using the BAM friction tester. The classification of the tested compounds results from the “UN Recommendations on the Transport of Dangerous Goods”.⁸ Concerning the impact sensitivity compound **7** is “less sensitive”, while **4** has to be classified as “sensitive” and therefore handled with special security measurements. In contrast **7** is insensitive towards friction while **4** is again classified as “sensitive”. With the trends of rising nitrogen content and heats of formation the sensitivities towards friction and impact are increased.

All salts were tested negative on their sensitivity against electrical discharge using a 20 kV tesla-coil spark device.

2.3. KOENEN TEST OF TRIAMINOGUANIDINIUM 1-METHYL-5-NITRIMINITETRAZOLATE

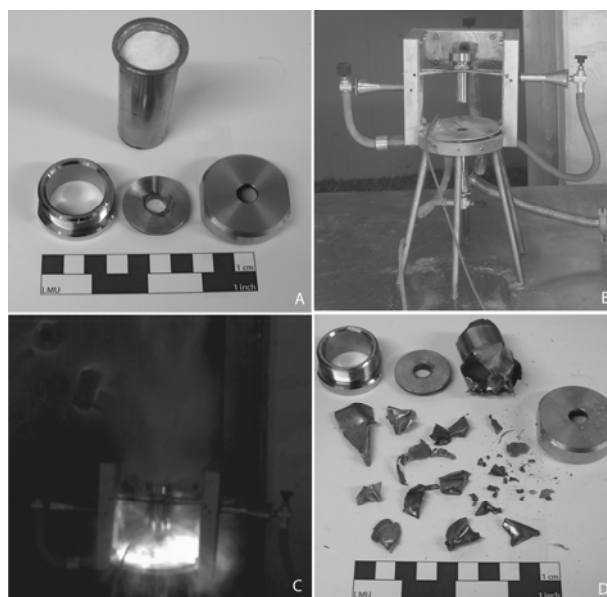


Figure 1 A) Steel sleeve loaded with 27 g of **4**. B) Koenen test setup showing four *Bunsen* burners. C) Moment of explosion filmed using a high speed camera (2500 frames s⁻¹) D) Result of the Koenen test showing the collected fragments.

Compound **4** was investigated according to its explosion performance under confinement using a “Koenen test” steel sleeve apparatus.^{10,11} The performance of the explosive can be related to the data obtained from the *Koenen* Test. Also the shipping classification of the substance can be determined and the degree of venting required to avoid an explosion during processing operations evaluated. The explosive is placed in a non-reusable open-ended flanged steel tube, which is locked up by a closing plate with variable orifice (0 – 10 mm), through which formed gaseous decomposition products are vented. A defined volume of 25 mL of the compound is loaded into the flanged steel tube and a threaded collar is slipped onto the tube from below. The closing plate is fitted over the flanged tube and secured with a nut. The explosion is initiated via thermal ignition using four *Bunsen* burners, which are started simultaneously. The test is completed when either rupture of the tube or no reaction is observed, after heating the tube for a minimal time period of at least 5 min. In case of the tube’s rupture the fragments are collected and weighed. The reaction is evaluated as an explosion if the

tube is destroyed into three or more pieces. The *Koenen* test was performed with 27 g of triaminoguanidinium 1-methyl-5-nitriminotetrazolate using a closing plate with an orifice of 10 mm. The first trial was successful indicated by the rupture of the steel tube into more than 15 fragments, which are shown in Fig. 1. TNT destroys the steel sleeve up to an orifice width of 6 mm, RDX even up to 8 mm.⁹ Compared to these applied explosives the performance of compound **4** is obviously better, although the calculated detonation parameters of RDX are slightly higher.

2.4. CONCLUSION

From the experimental study of 1,3,5-triaminoguanidinium 1-methyl-5-nitriminotetrazolate and 3,3'-bis-1,2,4-oxadiazol-5-onate salts the following conclusions can be drawn:^{12, 13}

- 1-Methyl-5-nitriminotetrazole can be easily deprotonated in aqueous solution using alkali hydroxides forming the corresponding alkali salts in nearly quantitative yields. These form the silver salt by the reaction with AgNO₃ in aqueous solutions.

- 3,3'-bis-1,2,4-oxadiazol-5-onate can be easily deprotonated in aqueous solution using alkaline earth metal hydroxides forming the corresponding earth metal salts in nearly quantitative yields.

- The nitrogen-rich 1-methyl-5-nitriminotetrazolate salt **4** can easily be obtained via metathesis reactions using silver 1-methyl-5-nitriminotetrazolate and the 1,3,5-triaminoguanidinium chloride in aqueous solution with high yields and good purity. An alternative synthesis route is the reaction of 1,3,5-triaminoguanidinium perchlorate with potassium 1-methyl-5-nitriminotetrazolate. This route eliminates the light sensitive silver salt. **4** can be recrystallized from water/ethanol mixtures resulting in colorless crystals.

- The 3,3'-bis-1,2,4-oxadiazol-5-onate salt **7** can easily be obtained via metathesis reactions using barium 3,3'-bis-1,2,4-oxadiazol-5-onate and the 1,3,5-triaminoguanidinium sulfate in aqueous solution with high yields and good purity. This route eliminates the light sensitive silver salt. **7** can be recrystallized from water/ethanol mixtures resulting in colorless crystals.

- A comprehensive analytical characterization of the physico-chemical properties and sensitivities of the endothermic compounds **4** and **7** are given. Although the salts are energetic materials with high nitrogen contents, they show good stabilities towards friction and impact and a good thermal stability. Especially **4** shows a well-defined melting point in the range from 120 ° to 195 °C, which depends on the number of existing hydrogen bonds, and temperatures of decomposition over 200 °C.

Compound **7** shows no melting point and a decomposition point slightly below 200 °C.

- Promising detonation parameters were calculated for **4** and **7** compared to common explosives like RDX. The performance (calculated values: $p_d = 273$ kbar; $v_d = 8770$ m s⁻¹) of triaminoguanidinium 1-methyl-5-nitriminotetrazolate (**4**) even successful in the *Koenen* test using a critical diameter of 10 mm qualifies it for further investigations concerning military applications. The performance (calculated values: $p_d = 231$ kbar; $v_d = 8104$ m s⁻¹) of triaminoguanidinium 3,3'-bis-1,2,4-oxadiazol-5-onate (**7**) are little decreased to RDX but accompanied by a very low temperature of explosion (2673 K) which would not be so effective as high explosive but suitable as erosion-reduced gun propellant.

2.5. EXPERIMENTAL PART

Caution! 1-Methyl-5-nitriminotetrazole and its salts are energetic materials with increased sensitivities towards shock and friction. Therefore proper security precautions (safety glass, face shield, earthed equipment and shoes, Kevlar® gloves and ear plugs) have to be applied synthesizing and handling the described compounds. Especially compounds described containing the azido or perchlorate group are extremely sensitive and have to be handled very carefully.

All chemicals and solvents were employed as received (Sigma-Aldrich, Fluka, Acros). ¹H, ¹³C, ¹⁴N and ¹⁵N NMR spectra were recorded using a JEOL Eclipse 270, JEOL EX 400 or a JEOL Eclipse 400 instrument. The chemical shifts quoted in ppm in the text refer to typical standards, such as trimethylsilane (TMS; ¹H, ¹³C) or nitromethane (¹⁴N, ¹⁵N). To determine the melting points of the described compounds a Linseis PT 10 DSC (heating rate: 5 °C per minute) was used. Raman spectra were recorded with a Perkin-Elmer Spektrum 2000R NIR FT-Raman instrument, which uses an Nd:YAG laser with a wavelength of 1064 nm. Infrared (IR) spectra were recorded using a Perkin-Elmer One FT-IR instrument with ATR unit. Bomb calorimetry was performed with a Parr 1356 Bomb calorimeter employing a Parr 207A oxygen bomb. To measure Elemental Analyses a Netsch STA 429 Simultaneous Thermal Analyzer was employed.

Triaminoguanidinium 1-methyl-5-nitriminotetrazolate (4): Potassium 1-methyl-5-nitriminotetrazolate (3.34 g, 0.02 mol) was dissolved in 20 mL water. Under constant stirring a solution of silver nitrate (3.38 g, 0.02 mol) in water was added. **3**, which started instantly to precipitate, was filtered and washed with small amounts of water. The wet powder was completely transferred into a reaction vessel, which contained a solution of triaminoguanidinium chloride (2.80 g, 0.02 mol) in water. Silver chloride started to precipitate immediately, indicating the successful course of the reaction. The silver chloride was

filtered off and the filtrate was collected in a volumetric reaction flask. The solvent was removed by a rotary evaporator. After recrystallization from water/ethanol colorless needles were obtained. (4.52 g, yield 91 %) M.p. 158 °C, 225 °C (dec.) (DSC, 5 deg/min); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3469 (w), 3371 (m), 3322 (vs), 3207 (s), 1676 (s), 1618 (w), 1507 (s), 1455 (vs), 1340 (vs), 1228 (s), 1194 (m), 1132 (m), 1107 (s), 1036 (m), 979 (m), 880 (m), 773 (m), 739 (m), 687 (m); Raman (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3331 (20), 3229 (12), 2986 (16), 1506 (100), 1462 (32), 1418 (17), 1295 (35), 1228 (11), 1108 (20), 1038 (94), 978 (12), 894 (21), 754 (18), 691 (23), 637 (10), 489 (17), 414 (13), 301 (21), 207 (18); ^1H NMR ([d6]-DMSO, 25 °C) δ = 8.60 (s, 3H, NH–NH₂), 4.50 (s, 6H, NH–NH₂), 3.67 (s, 3H, CH₃); ^{13}C NMR ([d6]-DMSO, 25 °C) δ = 159.6 (Tag⁺), 157.7 (CN₄), 33.1 (CH₃); ^{15}N NMR ([d6]-DMSO, 25 °C) δ = 4.45 (N3), -14.12 (N6), -18.29 (N2, t, $^3J_{\text{NH}}$ = 1.9 Hz), -71.15 (N4), -157.16 (N5), -168.38 (N1, d, $^2J_{\text{NH}}$ = 2.2 Hz), -289.13 (N7, $^1J_{\text{NH}}$ = 102.7 Hz), -329.66 (N8, $^1J_{\text{NH}}$ = 69.4 Hz); m/z (FAB⁺): 105 (cation); m/z (FAB⁻): 143 (anion); EA (C₃H₁₂N₁₂O₂, M = 248.21) calc. C 14.52, H 4.87, N 67.72 %; found: C 14.52, H 4.77, N 67.45 %; BAM-Drophammer: > 6 J; BAM-Friction Test: > 240 N; $\Delta U_{\text{comb.}}$: 14.01 kJ g⁻¹.

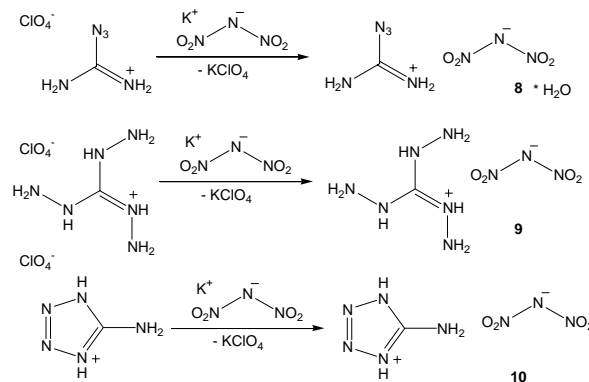
Triaminoguanidinium 3,3'-bis-1,2,4-oxadiazol-5-onate(47) 2.45 g (7.00 mmol) barium 3,3'-bisoxadiazol-5-onate dihydrate was suspended in 80 mL of a water : ethanol mixture (3:1) while boiling and a solution of 2.14 g (7.00 mmol) triaminoguanidinium sulfate in 20 mL water was added. The mixture was heated for 30 min at 100 °C and stirred for further 3 h at room temperature. After one hour of reaction time the pH-value was checked and little sulfuric acid was added to obtain pH 5. The barium sulfate precipitates and was filtered and washed with water. The solvent of the filtrate was evaporated and the colorless product was gained. (2.11 g, yield 80 %). T(dec) 183 °C (DSC 5 deg/min); IR (ATR, cm^{-1}) $\tilde{\nu}$ = 3427 vs, 3404 s, 3326 m, 3155 vs, 3087 m, 1702 s, 1663 vs, 1474 m, 1280 m, 1212 m, 1099 s, 1083 s, 1019 w, 943 w, 880 w, 776 w, 610 w; Raman (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3279 (27), 1684 (19), 1577 (68), 1561 (54), 1508 (24), 1216 (31), 1077 (17), 975 (100), 945 (41), 910 (32), 779 (42), 740 (16), 605 (19), 552 (17), 525 (28), 411 (40), 338 (28), 271 (18), 242 (21), 146 (13); m/z (FAB⁺) 105.1 (cation); m/z (FAB⁻) = 169.0 (anion); BAM-Drophammer: >100 J; BAM-Friction Test: > 218 N.

3. DINITRAMIDE SALTS

3.1. SYNTHESSES

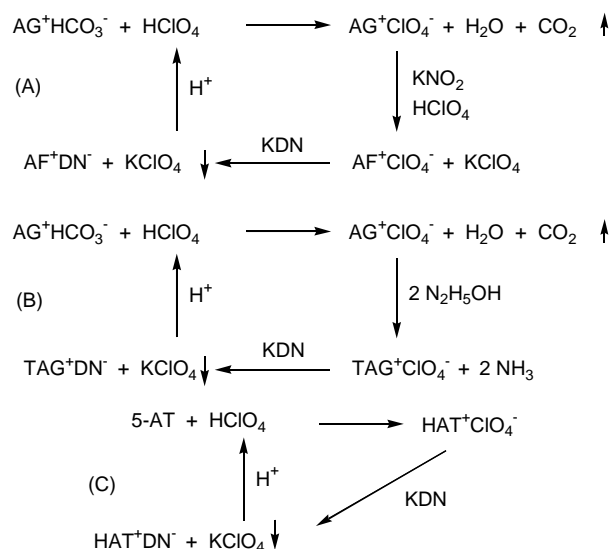
Azidoformamdidinium dinitramide (8), triaminoguanidinium dinitramide (9) as well as 5-aminotetrazolium dinitramide (10) were prepared

according to the new syntheses presented in scheme 1. The impetus of the reaction of azidoformamdidinium perchlorate (AF-ClO₄), 1,3,5-triaminoguanidinium perchlorate (TAG-ClO₄) and 5-aminotetrazolium perchlorate (HAT-ClO₄) with potassium dinitramide (KDN) is the precipitation of low soluble KClO₄ which can be separated by filtration. AF-ClO₄, TAG-ClO₄ and HAT-ClO₄ were prepared in our research labs according to recently developed new syntheses.¹⁴



Scheme 3 Synthesis of azidoformamdidinium dinitramide monohydrate (8), triaminoguanidinium dinitramide (9), 5-aminotetrazolium dinitramide (10)

The separated KClO₄ side-product can easily be converted back into the free acid and re-used in the synthetic cycle making more AF-ClO₄, TAG-ClO₄, and HAT-ClO₄ starting material (scheme 2). Thus, the new syntheses not only afford the desired products in high yield but also fulfill the sustainability criteria of the preparation cycle.



Scheme 4 Reaction cycle for the preparation of 8 (A), 9 (B), 10 (C). (AG: aminoguanidinium)

3.2. COMPUTATIONAL STUDY

Due to the highly energetic character of **8** - **10**, bomb calorimetric measurements could only performed with small amounts, consequently doubtful combustion energies were obtained. Therefore an extensive computational study was accomplished which is presented in the following. All calculations were carried out using the Gaussian G03W (revision B.03) program package.¹⁵ The enthalpies (H) and free energies (G) were calculated using the complete basis set (CBS) method of Petersson and coworkers in order to obtain very accurate energies. The CBS models use the known asymptotic convergence of pair natural orbital expressions to extrapolate from calculations using a finite basis set to the estimated complete basis set limit. CBS-4 begins with a HF/3-21G(d) geometry optimization; the zero point energy is computed at the same level. It then uses a large basis set SCF calculation as a base energy, and a MP2/6-31+G calculation with a CBS extrapolation to correct the energy through second order. A MP4(SDQ)/6-31+(d,p) calculation is used to approximate higher order contributions. In this study we applied the modified CBS-4M method (M referring to the use of Minimal Population localization) which is a re-parametrized version of the original CBS-4 method and also includes some additional empirical corrections.^{16, 17} The enthalpies of the gas-phase species M were computed according to the atomization energy method (eq. 1) (Tab. 1-3).^{18,19}

Equation 1. $\Delta_f H^\circ(\text{g}, \text{M}, 298) = H(\text{Molecule}, 298) - \sum H^\circ(\text{Atoms}, 298) + \sum \Delta_f H^\circ(\text{Atoms}, 298)$

Table 1. CBS-4M results

	p.g.	$-H^{298} / \text{a.u.}$	$-G^{298} / \text{a.u.}$	NIMAG
TAG ⁺	C ₃	371.197775	371.236698	0
DN ⁻	C ₂	464.499549	464.536783	0
AF ⁺	C _s	313.533549	313.570115	0
HAT ⁺	C _s	313.534215	313.567694	0
H		0.500991	0.514005	0
C		37.786156	37.803062	0
N		54.522462	54.539858	0
O		74.991202	75.008515	0

Table 2. Literature values for atomic $\Delta_f H^\circ_{\text{f}} / \text{kcal mol}^{-1}$

	Ref. ²⁰	NIST ²¹
H	52.6	52.1
C	170.2	171.3

N	113.5	113.0
O	60.0	59.6

Table 3. Enthalpies of the gas-phase species M.

M	M	$\Delta_f H^\circ(\text{g}, \text{M}) / \text{kcal mol}^{-1}$
TAG ⁺	C(NH-NH ₂) ₃ ⁺ , CH ₉ N ₆ ⁺	+208.8
DN ⁻	N(NO ₂) ₂ ⁻ , N ₃ O ₄ ⁻	-29.6
AF ⁺	(H ₂ N) ₂ CN ₃ ⁺ , CH ₄ N ₅ ⁺	+235.4
HAT ⁺	CH ₄ N ₅	+235.0

The lattice energies (U_L) and lattice enthalpies (ΔH_L) were calculated from the corresponding molecular volumes (Tab. 4) according to the equations provided by Jenkins et al.²² and are summarized in Tab. 5.

Table 4. Molecular volumes.

	$V_M / \text{\AA}^3$	V_M / pm^3
DN ⁻	89 ^a	0.089 ^c
[TAG] ⁺	108 ^b	0.108 ^b
[HAT] ⁺	69 ^c	0.069 ^b
[NH ₄][DN]	110 ²³	0.110
[TAG][DN]	215 ^e	0.215 ²⁴
[AF][DN]	174 ^f	0.174 ^e

[a] this work, back-calculated from V(ADN) using the molecular volume for NH₄⁺ from the literature; [b] this work, back-calculated and averaged from V([TAG][NO₃]) and V([TAG][Cl]) using the molecular volumes for Cl⁻ and NO₃⁻; [c] The molecular volume of [HAT]⁺ was calculated from the molecular volume of [HAT][NO₃] - V_M(NO₃⁻); [e] from single crystal X-ray data; [f] The molecular volume of anhydrous [AF][DN] was calculated from the experimental volume of [AF][DN]·H₂O - V_M(H₂O, hydrate).

Table 5. Lattice energies and lattice enthalpies.

	V_M / nm^3	$U_L / \text{kJ mol}^{-1}$	$\Delta H_L / \text{kJ mol}^{-1}$	$\Delta H_L / \text{kcal mol}^{-1}$
[TAG][DN]	0.215	495.4	500.4	119.6
[AF][DN]	0.174	524.0	529.0	126.4
[HAT][DN]	0.172	525.6	530.6	126.8

With the calculated lattice enthalpies (Tab. 5) the gas-phase enthalpies of formation (Tab. 4) were converted into the solid state (standard conditions) enthalpies of formation (Tab. 6). These molar standard enthalpies of formation (ΔH_m) were used to calculate the molar solid

state energies of formation (ΔU_m) according to eq. (2) (Tab. 7).

Equation 2. $\Delta U_m = \Delta H_m - \Delta n RT$

(Δn being the change of moles of gaseous components)

Table 6. Enthalpies of formation of the solid species M.

	$\Delta_f H^\circ(s, M) / \text{kcal mol}^{-1}$	$\Delta_f H^\circ(s, M) / \text{kcal mol}^{-1}, \text{lit. value}$
[TAG][DN]	+59.6	44.0 [4]
[AF][DN]	+79.4	59.8 [4]
[HAT][DN]	+78.6	

Table 7. Solid state energies of formation ($\Delta_f U^\circ$).

	$\Delta_f H^\circ(s) / \text{kcal mol}^{-1}$	Δn	$\Delta_f U^\circ(s) / \text{kcal mol}^{-1}$	M / g mol ⁻¹	$\Delta_f U^\circ(s) / \text{kJ kg}^{-1}$
[TAG][DN]	+59.6	-11	66.1	211.1	1310.1
[AF][DN]	+79.4	-8	+84.0	192.1	1829.6
[HAT][DN]	+78.6	-8	83.3	192.1	+1813.3

The calculation of the detonation parameters was performed with the program package EXPLO5 (version 5.02).²⁵ The program is based on the chemical equilibrium, steady-state model of detonation. It uses the Becker-Kistiakowsky-Wilson's equation of state (BKW EOS) for gaseous detonation products and Cowan-Fickett's equation of state for solid carbon.^{26,27} The calculation of the equilibrium composition of the detonation products is done by applying modified White, Johnson and Dantzig's free energy minimization technique. The program is designed to enable the calculation of detonation parameters at the CJ point. The BKW equation in the following form was used with the BKWN set of parameters ($\alpha, \beta, \kappa, \theta$) as stated below the equations and X_i being the mol fraction of i -th gaseous product, k_i is the molar covolume of the i -th gaseous product:²⁸

Equation 3. $pV / RT = 1 + x e^{\beta x}$

$$x = (\kappa \sum X_i k_i) / [V (T + \theta)]^\alpha$$

$$\alpha = 0.5, \beta = 0.176, \kappa = 14.71, \theta = 6620.$$

The detonation parameters calculated with the EXPLO5 program using the experimentally determined densities (X-ray) are summarized in Table 8.

3.3. SENSITIVITIES

For initial safety testing, the impact and friction sensitivities as well as the electrostatic sensitivity were determined.²⁹ The impact sensitivity tests were carried out according to STANAG 4489³ modified according to instruction⁴ using a BAM (Bundesanstalt für Materialforschung)⁵ drophammer.⁶ The friction sensitivity tests were carried out according to STANAG 4487^[51] modified according to instruction⁷ using the BAM friction tester. Compound **8** is very sensitive towards impact (2 J) and also very friction sensitive (7 N). **9** and **10** are also very sensitive towards impact (**9**: 3 J, **10**: 2 J) and friction (**9**: 24 N, **10**: 20 N) and therefore compounds **8** – **10** are classified, according to the “UN Recommendations on the transport of dangerous goods”, as “very sensitive” in both categories.^[53]

The electrostatic sensitivity tests were carried out using an electric spark tester ESD 2010EN (OZM Research) operating with the “Winspark 1.15 software package”.²⁹ The electrical spark sensitivities were determined to be 930 (**8**), 790 mJ (**9**) and 750 mJ (**10**).

3.4. KOENEN TEST OF TRIAMINOGUANIDINIUM DINITRAMIDE (**9**)

Compound **9** was investigated according to its explosion performance under confinement using a “Koenen” steel sleeve apparatus.^{10,11} Also the shipping classification of the substance can be determined and the degree of venting required to avoid an explosion during processing operations evaluated. The explosive is placed in a non-reusable open-ended flanged steel tube, which is locked up by a closing plate with variable orifice (0 – 10 mm), through which formed gaseous decomposition products are vented. A defined volume of 25 mL of the compound is loaded into the flanged steel tube and a threaded collar is slipped onto the tube from below. The closing plate is fitted over the flanged tube and secured with a nut. The explosion is initiated via thermal ignition using four *Bunsen* burners, which are started simultaneously.

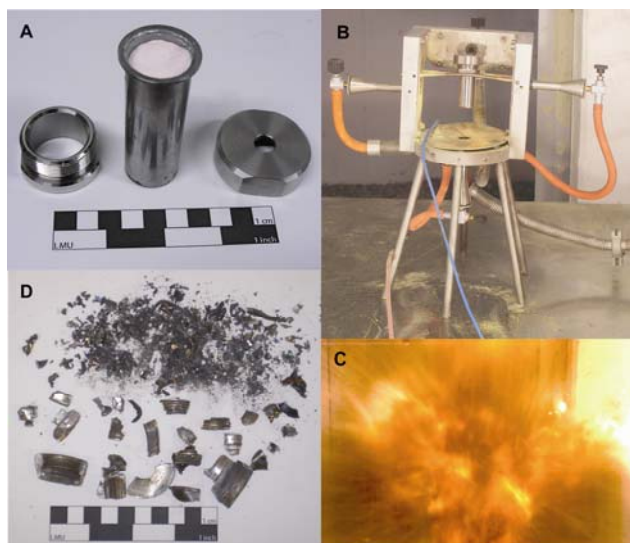


Figure 2 A) Steel sleeve loaded with 23.6 g of **9**. B) Koenen test setup showing four Bunsen burners. C) Moment of explosion filmed using a high speed camera (4000 frames s⁻¹) D) Result of the Koenen test showing the collected fragments.

The test is completed when either rupture of the tube or no reaction is observed, after heating the tube for a minimal time period of at least 5 min. In case of the tube's rupture the fragments are collected and weighed. The reaction is evaluated as an explosion if the tube is destroyed into three or more pieces. TNT (trinitrotoluene) destroys the steel sleeve up to an orifice width of 6 mm, RDX (Royal Demolition Explosive) even up to 8 mm. The following *Koenen* test was performed with 23.6 g of triaminoguanidinium dinitramide (**9**) using a closing plate with an orifice of 10 mm. The first trial was successful indicated by the rupture of the steel tube into powder like pieces, which are shown in Fig. 8. Also the apparatus was destroyed violently and was found two meters away from its explosion position. The explosion occurred within 1 ms, which was observed using a high speed camera (4000 frames s⁻¹). The experimental detonation velocity was also estimated to be close to 9000 m s⁻¹.

3.5. CONCLUSIONS

From this combined experimental and theoretical study the following conclusions can be drawn:^{31, 32}

(i) Azidoformamidinium dinitramide (AF_DN, **8**), triaminoguanidinium dinitramide (TAG_DN, **9**) and 5-aminotetrazolium dinitramide (HAT_DN, **10**) were prepared in high yields from the reaction of potassium dinitramide and azidoformamidinium perchlorate, triaminoguanidinium perchlorate and 5-aminotetrazolium perchlorate respectively.

(ii) The explosive and detonation parameters of AF_DN, TAG_DN and HAT_DN were obtained from a combined experimental and computational study and are summarized in Table 8. Comparison with the literature values reported for RDX it can be concluded that especially triaminoguanidinium dinitramide (TAG-DN, **9**) may also be a valuable ingredient as an energetic filler in high explosive compositions.

3.6. EXPERIMENTAL PART

CAUTION! Azidoformamidinium-, triaminoguanidinium and 5-aminotetrazolium perchlorate as well as the dinitramides **1** - **3** are highly energetic compounds with increased sensitivities against various stimuli. Although we had no problem during the syntheses, proper protective measures (safety glasses, face shield, leather coat, earthened equipment and shoes, Kevlar® gloves and ear plugs) should be used.

Azidoformamidinium dinitramide (8): To a solution of azidoformamidinium perchlorate (1.86 g, 10 mmol) in 15 mL water a solution of potassium dinitramide (1.45, 10 mmol) in 20 mL water was added drop wise. After stirring for one hour at room temperature the precipitate formed was filtered off and the solution was evaporated to dryness. The colorless crude product was recrystallized from a small amount of ethanol. The product **8** was obtained as its monohydrate (1.89 g, 90 %). **m.p.:** 120 °C (dec.); **IR** (ATR): ν = 3615 (s), 3541 (m), 3330 (vs), 3248 (s), 3136 (s), 2184 (s), 2127 (m), 1676 (s), 1652 (s), 1623 (m), 1523 (s), 1490 (s), 1447 (s), 310 (w), 1250 (m), 1187 (s), 1075 (w), 1018 (m), 898 (w), 743 (m), 647 (m); **Raman** (1064 nm): ν = 3326 (6), 2184 (40), 2115 (10), 1647 (6), 1503 (12), 1454 (17), 1321 (100), 1232 (7), 1172 (11), 1107 (13), 1014 (9), 962 (16), 904 (41), 824 (47), 763 (7), 660 (16), 500 (19), 485 (19), 471 (24), 298 (24) 218 (43); **¹H NMR** (D₂O): δ (ppm) = 8.50 (br, NH₂); **¹³C NMR** (D₂O): δ (ppm) = 159.9 (C1); **¹⁵C NMR** (D₂O): δ (ppm) = -13.2 (NO₂), -58.6 (N(NO₂)₂), -137.7 (-N=N=N₇), -152.0 (-N=N₆=N), -291.1 (NH₂) -305.8 (-N₆=N=N); **m/z** (FAB⁺): 86; (FAB⁻): 106; **EA** (CH₉N₉O₄, 210.11): calc. C 5.72, H 2.88, N 53.33 %; found: not determinable; **BAM drophammer:** 2 J, **BAM friction test:** 7 N. **ESD:** 670 mJ.

Triaminoguanidinium dinitramide (9): Triaminoguanidinium perchlorate (20.47 g, 0.10 mol) was dissolved in 70 mL of water. To this a solution of potassium dinitramide (14.51 g, 0.10 mol) in 50 mL of water was added drop wise while KClO₄ started to precipitate. The mixture was stirred for 30 min and was filtered off. The solution was evaporated at 40 °C and the residue was recrystallized hot from ethanol yielding TAG-DN as colorless needles (17.3 g, 82 %). **m.p.:** 80 °C, 180 °C (dec.); **IR** (KBr): ν = 3360 (s), 3299 (vs), 3273 (vs), 1676 (s), 1491 (s), 1414 (m), 1362 (w), 1325 (m), 1155 (m), 1131 (s), 989 (m), 947 (s), 916 (s), 821 (m), 759 (m),

740 (m), 639 (w); **Raman** (1064 nm): $\nu = 3361$ (28), 3311 (35), 1687 (11), 1513 (20), 1430 (19), 1326 (100), 1200 (7), 1169 (7), 1140 (9), 953 (26), 895 (32), 825 (65), 638 (10), 488 (32), 452 (12), 417 (17), 313 (22), 261 (19); **^1H NMR** ($\text{D}_6\text{-DMSO}$): δ (ppm) = 8.57 (3H, s, -NH-), 4.45 (6H, s, -NH₂); **^{13}C NMR** ($\text{D}_6\text{-DMSO}$): δ (ppm) = 159.6 (C1); **^{15}C NMR** ($\text{D}_6\text{-DMSO}$): δ (ppm) = -10.3 (NO_2), -55.3 ($\text{N}(\text{NO}_2)_2$), -289.2 (NH, d, $^1\text{J}_{\text{N-H}} = 103$ Hz), -329.8 (NH₂, t, $^1\text{J}_{\text{N-H}} = 73$ Hz); **m/z** (FAB^+): 105; (FAB^-): 106; **EA** ($\text{CH}_6\text{N}_7\text{O}_5$, 211.14): calc. C 5.69, H 4.30, N 59.70 %; found: C 5.67, H 4.01, N 58.66 %; **BAM drophammer**: 3 J, **BAM friction test**: 24 N. **ESD**: 8 mJ.

5-Aminotetrazolium dinitramide (10): A solution of 5-Aminotetrazolium perchlorate (5.56 g, 30 mmol) in 15 mL water was combined with a solution of potassium dinitramide (4.35 g, 30 mmol) in 25 mL water. 10 mL of was added and the mixture was stirred for 20 min. The potassium perchlorate precipitated was filtered off and the solution was evaporated to dryness using high vacuum (5.36 g, 92 %). Single crystals suitable for X-ray diffraction were obtained by recrystallization from ethanol. **m.p.**: 85 °C, 117 °C (dec.); **IR** (KBr): $\nu = 3332$ (s), 3262 (s), 3154 (s), 1698 (s), 1535 (s), 1430 (s), 1343 (m), 1291 (m), 1199 (s), 1177 (vs), 1071 (m), 1023 (s), 997 (m), 953 (m), 826 (w), 761 (w), 731 (m), 710 (w), 624 (m), 543 (w), 470 (w); **Raman** (1064 nm): $\nu = 3315$ (6), 1692 (5), 1594 (6), 1577 (8), 1536 (8), 1449 (14), 1391 (10), 1325 (100), 1163 (9), 1066 (43), 1032 (10), 1017 (11), 958 (15), 824 (48), 749 (59), 490 (29), 416 (25), 319 (17); **^1H NMR** ($\text{D}_6\text{-DMSO}$): δ (ppm) = 10.80 (4H, s); **^{13}C NMR** ($\text{D}_6\text{-DMSO}$): δ (ppm) = 152.4 (C1); **^{14}C NMR** ($\text{D}_6\text{-DMSO}$): δ (ppm) = -11 (NO_2), **m/z** (FAB^+): 86; (FAB^-): 106; **EA** ($\text{CH}_4\text{N}_8\text{O}_4$, 192.09): calc. C 6.25, H 2.10, N 58.33 %; found: C 6.11, H 2.39, N 58.01 %; **BAM drophammer**: 2 J, **BAM friction test**: 20 N. **ESD**: 750 mJ.

4. CONCLUSIONS

The introduced new high explosives display exceptional thermal behaviors and performances. The triaminoguanidinium 1-methyl-5-nitriminotetrazolate (**4**) as well as the triaminoguanidinium dinitramide (**9**) are promising candidates for application as environmentally friendly replacement for toxic RDX. Thus warfighters' health will not be affected during training more than needed. The triaminoguanidinium 3,3'-bis-1,2,4-oxadiazol-5-onate (**7**) is promising for application as less erosive gun propellant. The use of those could minimize the cost of repairs and missions are less endangered through malfunction of equipment.

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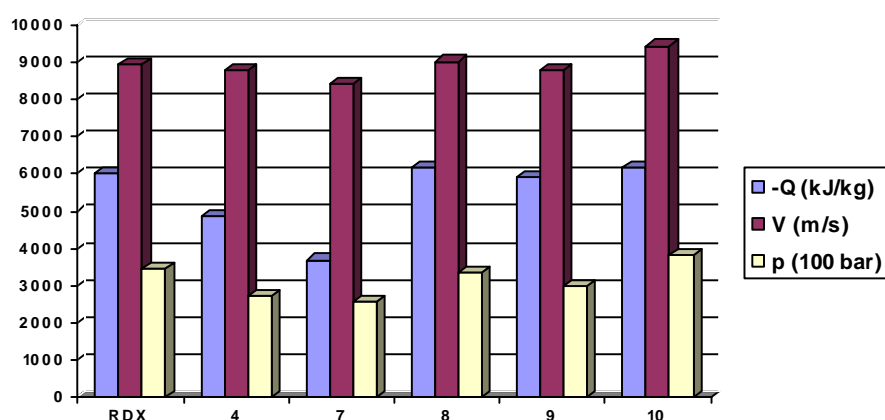
Financial support of this work by the Ludwig-Maximilian University of Munich (LMU), the European Research Office (ERO) of the U.S. Army Research Laboratory (ARL) and ARDEC (Armament Research, Development and Engineering Center) under contract nos. N 62558-05-C-0027, R&D 1284-CH-01, R&D 1285-CH-01, 9939-AN-01 & W911NF-07-1-0569 is gratefully acknowledged. The authors acknowledge collaborations Dr. M. Krupka (OZM Research, Czech Republic) in the development of new testing and evaluation methods for energetic materials and with Dr. M. Suceca (Brodarski Institute, Croatia) in the development of new computational codes to predict the detonation parameters of high-nitrogen explosives. We are indebted to and thank Dr. Betsy M. Rice (ARL, Aberdeen, Proving Ground, MD) for many helpful and inspired discussions and support of our work.

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Table 8. Energetic properties of compounds **4**, **7**, **8-10** and RDX for comparison

	RDX	TAG 1- MeAtNO ₂ (4)	TAG OD (7)	AF_DN (8)	TAG_DN (9)	HAT_DN 10)
Molecular Mass (g mol ⁻¹)	222.1 ¹⁹	248.25	378.31	192.09	211.2	192.09
Impact sensitivity (J)	7 ¹⁹	6	100	2	3	2
Friction sensitivity (N)	120 ¹⁹	240	218	7	24	20
Electrical discharge (J)	0.15- 0.2 ²⁰	not determined	1.5	0.93	0.79	0.75
Crit. diam. of steel sleeve test (mm)	8 ¹⁹	≥10	not determined	not determined	≥10	not determined
Nitrogen content (%)	37.8 ¹⁹	67.72	59.2	58.33	59.7	58.33
Oxygen Balance (%)	-21.6 ¹⁹	-64.46	-71.9	0	-18.9	0
T _{dec.} (°C)	ca. 213 ¹⁹	>210	>197	> 120	> 180	> 117
Density (g cm ⁻³)	1.82 ¹⁹	1.57.	1.724	1.754	1.628	1.856
-Δ _c H (kJ mol ⁻¹)	2105	3465			2027	
Δ _f H _m ^o (kJ mol ⁻¹)	66.5 ¹⁹	569	223	332	250	329
Δ _f U ^o (kJ kg ⁻¹)	1310	2423	713	1830 ^b	1773	1813
calculated values by						
EXPLO5						
- Δ _E U _m ^o (J g ⁻¹)	-5902	4888	-3699	-6168	-6360	6186
Explosion temp. (T _E) (K)	3986	3210	2673	4710	4231	4657
Det. pressure (p) (kbar)	299	273	231	338	320	384
Det. velocity (D) (m s ⁻¹)	8796	8770	8104	9013	9039	9429
Gas vol. [mL g ⁻¹]	932	886	848	823	932	822

**Figure 3** Important detonation parameters for compounds **4**, **7**, **8-10** and for RDX for comparison.

- [8] Impact: Insensitive > 40 J, less sensitive ≥ 35 J, sensitive ≥ 4 J, very sensitive ≤ 3 J; friction: Insensitive > 360 N, less sensitive $= 360$ N, sensitive < 360 N a. > 80 N, very sensitive ≤ 80 N, extreme sensitive ≤ 10 N; According to the UN Recommendations on the Transport of Dangerous Goods (+) indicates: not safe for transport.
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